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Citation style: Dzionek Anna, Wojcieszyńska Danuta, Guzik Urszula. (2016). Natural carriers in bioremediation: a review. "Electronic Journal of Biotechnology" (Vol. 23, [September] (2016), s. 28-36), doi 10.1016/j.ejbt.2016.07.003

Electronic Journal of Biotechnology 23 (2016) 28–36

Contents lists available at ScienceDirect

Electronic Journal of Biotechnology

Review

Natural carriers in bioremediation: A review

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A R T I C L E I N F O

Article history:
Received 5 April 2016
Accepted 27 July 2016
Available online 12 August 2016

Keywords:
Adsorption
Bioethanol production
Contamination
Heavy metals
Immobilization
Immobilized microorganisms
Natural carriers
Wine alterations
Wood barrels
Xenobiotics

A B S T R A C T

Bioremediation of contaminated groundwater or soil is currently the cheapest and the least harmful method of removing xenobiotics from the environment. Immobilization of microorganisms capable of degrading specific contaminants significantly promotes bioremediation processes, reduces their costs, and also allows for the multiple use of biocatalysts. Among the developed methods of immobilization, adsorption on the surface is the most common method in bioremediation, due to the simplicity of the procedure and its non-toxicity. The choice of carrier is an essential element for successful bioremediation. It is also important to consider the type of process (*in situ* or *ex situ*), type of pollution, and properties of immobilized microorganisms. For these reasons, the article summarizes recent scientific reports about the use of natural carriers in bioremediation, including efficiency, the impact of the carrier on microorganisms and contamination, and the nature of the conducted research.

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Peer review under responsibility of Pontificia Universidad Católica de Valparaíso.

http://dx.doi.org/10.1016/j.ejbt.2016.07.003

1. Introduction

The twentieth century went down in history as a period of extremely dynamic civilizational and technological development. Industrialization, wars, and intensive use of large-scale heavy metals and synthetic xenobiotics led to many environmental problems [1,2].

The contamination of the environment by petroleum products, pharmaceutical compounds, chloro- and nitrophenols and their derivatives, polycyclic aromatic hydrocarbons, organic dyes, pesticides and heavy metals is a serious problem [3,4,5,6,7,8,9]. These pollutants enter the environment by different ways. For example, one of the major consequences of the armed conflict between Iraq and Kuwait was the release into the environment millions of barrels of crude oil. After the war ended, scientists began numerous studies aimed at the removal of oil from the contaminated environment. Other sources of crude oil in ecosystems are accidental oil spills. One of the biggest marine disasters took place in Mexico in 2010, and it resulted in the spewing out of about 2.8 million barrels of crude oil from the British Petroleum (BP) oil rig Deepwater Horizon into the sea [10,11].

Pesticides are other serious pollutants present in soils. USEPA reported that in 2007, global consumption of pesticides for agricultural purposes was 2.36 million tonnes [12]. These compounds, used in bulk for long periods of time in a limited area, lead to serious disorders in indigenous microflora and humans, because pesticides are also toxic to non-target organisms [12,13,14]. Moreover, many metabolites of pesticide biodegradation are also toxic and constitute priority pollutants. For example, the major metabolites of parathion and 2,4-dichloropenoxy acetic acid biodegradation are *p*-nitrophenol and 2,4-dichlorophenol, respectively [9,15,16,17,18].

It has been reported that many microorganisms are able to biodegrade different pollutants [4,5,7,8,19,20]. However, the biodegradation rate depends on the physiological state of the microorganisms, which are sensitive to variable environmental factors. It is known that immobilization improves microorganisms' resistance to unfavourable environmental impacts [6,8].

The main purpose of this review is to present and discuss the latest reports about the natural carriers in the processes of bioremediation by immobilized cells. In the article immobilization methods for bioremediation are also presented.

2. Bioremediation methods

In 1930 Tausz and Donath [21] presented the idea of using microorganism to clean soil contaminated with petroleum derivatives, giving rise to biodegradation processes. Today, bioremediation is a commonly used method to restore the natural and useful values of contaminated sites by microorganism able to degrade, transform, or chelate various toxic compounds [22]. Microorganisms can break down organic pollutants by using them as a source of carbon and energy, or by cometabolism. Heavy metals cannot be degraded or destroyed biologically and undergo transformation from one oxidative state or organic complex to another. It changes their water solubility and decreases their toxicity [22,23].

Bioremediation is eco-friendly, non-invasive, cheaper than conventional methods, and it is a permanent solution that can end with degradation or transformation of environmental contaminants into harmless or less toxic forms [23,24,25,26]. Soil bioremediation can be carried out at the place of contamination (*in situ*), or in a specially prepared place (*ex situ*). *In situ* technology is used when there is no possibility to transfer polluted soil, for example when contamination affects an extensive area [26,27,28].

There are three basic methods of *in situ* bioremediation with microorganisms: natural attenuation, biostimulation, and bioaugmentation [24,29,30].

Natural attenuation is connected with the degradation activities of indigenous microorganisms. This method avoids damaging the habitat, allows ecosystem revert to its original condition and enables detoxification of toxic compounds [24,31].

Removal of contaminations by the natural attenuation takes a long time because degrading microorganisms in soil represent only about 10% of the total population. The increase of bioremediation efficiency *in situ* may be realized in the bioaugmentation process, in which the specific degraders are introduced into the soil [30,31]. This method is applied when the indigenous microflora are unable to break down pollutants, or when the population of microorganisms capable of degrading contaminants is not sufficiently large. To make the process of bioaugmentation successful, microorganisms introduced into the polluted environment as a free or immobilized inoculum should be able to degrade specific contamination and survive in a foreign and unfriendly habitat, be genetically stable and viable, and move through the pores in the soil. Microorganisms can be previously isolated from the contaminated soil and propagated, or their functional ability can be enhanced in the laboratory. Nonindigenous strains or genetically modified microorganisms (GMM) can also be incorporated into the remediated soil [31,32,33,34]. However, the result of bioaugmentation depends on the interaction between exogenous and indigenous populations of microorganisms because of the competition, mainly for nutrients [31].

To accelerate *in situ* bioremediation processes, biostimulation is used in order to modify the physical and chemical parameters of the soil. For this purpose, compounds such as nutrients (*e.g.* biogas slurry, manure, spent mushroom compost, rice straw and corncob) or electron acceptors (phosphorus, nitrogen, oxygen, carbon) are introduced into the soil [29,30,32,35].

Because *in situ* processes are out of hand it is difficult to predict the effect of remediation of contaminated sites [28]. *Ex situ* methods allow more efficient removal of pollutants, by controlling the physico-chemical parameters, resulting in a shortening of the total time of reclamation. These advantages outweigh *ex situ* methods' disadvantages such as additional cost and risk connected with the possibility of dispersion of the contamination during transport. During the *ex situ* processes contaminated medium is excavated or extracted and moved to the process location. Liquids can be clean in constructed wetlands while semi-solid or solid wastes in slurry bioreactors. Solid contaminations are biodegraded through land farming, composting and biopiles [26,28,36,37].

Constructed wetlands are used with success in the treatment of wastewater derived from domestic, industrial or agricultural sources [38]. They require the competition of microbes (bioremediation) and plant (phytoremediation). Microorganisms degrade or sorb organic substance present in the water undergoing treatment. Plants are used to remove, transfer or stabilize contaminants through metabolism, accumulation, phytoextraction or immobilization at interface of roots and soil [37]. Bioremediation processes in slurry bioreactors can be performed under aerobic or anaerobic conditions [28]. These systems utilize naturally occurring microorganisms or strains possessing specific metabolic capabilities to transform toxic compounds [27]. Slurry bioreactors are one of the best applied technologies used in the bioremediation of contaminated soils because they undergo under controlled operating conditions. It allows for the enhancement of microorganisms activity [27,39,40].

Landfarming is one of the most widely used soil bioremediation technologies. In this technology, excavated contaminated soils are spread out in a thin layer on the ground surface. Aerobic microbial activity within the soil is stimulated through the aeration and addition of minerals, nutrients and moisture [41,42]. Landfarming is a relatively simple technology however it is inexpensive and effective for easily biodegradable contaminants only at low concentration [28,37,41,42,43]. Composting is a controlled biological process that treats of agricultural and municipal solid wastes and sewage sludge using microorganisms under thermophilic and aerobic conditions [28,37]. Through composting, it is possible to reduce the volume of residues in landfills.

Biodegradation of solid contaminants takes place mainly as a result of oxidation and hydrolysis. The optimum temperature for growth of microorganisms engaged in composting is in the range of 40 to 70°C. The risk of contamination by pathogens is small, because most of them are inactivated at 70°C. A key factor during composting is microbial accessibility to the pollutants and the characteristics of the amending agents. This method is eco-friendly, has simple protocols, allows the control of large volumes of waste and ends with the total mineralization of pollutants [26,44,45]. Composting has been applied to bioremediation of soils contaminated with petroleum hydrocarbons, solvents, chlorophenols, pesticides, herbicides, polycyclic aromatic hydrocarbons and nitro-aromatic derivatives [28,37,46]. More advanced systems of composting are biopiles that are more expensive but enable more effective control of the process and its higher efficiency [28]. It is possible as the aerated composted piles are equipped with the dissolved oxygen, moisture and nutrient control systems and the proper aeration is forced by vacuum or injection system. This technology has been used for remediation of petroleum-contaminated soil [28,37,46].

3. Immobilization methods

In recent times, bioremediation processes more and more often employ immobilization methods. Immobilization is defined as limiting the mobility of the microbial cells or their enzymes with a simultaneous preservation of their viability and catalytic functions [47,48,49,50,51]. This process may use the natural ability of microorganisms to form biofilms on the surface of various materials, which is commonly observed in the environment. Immobilization significantly reduces costs of bioremediation processes and improves their efficiency. This method brings many benefits to bioremediation, such as higher efficiency of pollutant degradation, multiple use of biocatalysts, reduced costs — the stage of cell filtration is eliminated, ensuring a stable microenvironment for cells/enzymes, a reduced risk of genetic mutations, ensured resistance to shear forces present in bioreactors, increased resistance of biocatalysts to adverse environmental conditions and heavy metals, increased biocatalyst survival during storage, and increased tolerance to high pollutant concentrations [1,47,51,52].

There are five main techniques of immobilization: adsorption, binding on a surface (electrostatic or covalent), flocculation (natural or artificial), entrapment, and encapsulation (Fig. 1). Flocculation does not require carriers, and therefore will not be discussed [1,47].

3.1. Adsorption

Immobilization of microbial cells and enzymes by adsorption takes place through their physical interaction with the surface of water-insoluble carriers. This method, commonly used in bioremediation processes, is quick, simple, eco-friendly and cost-effective. Adsorption on a carrier surface is achieved by the formation of weak bonds. For that reason there is a high probability of cells leaking from the carrier into the environment, and this method is not used for GMM immobilization [1,53,54].

3.2. Binding on a surface

Electrostatic binding on a surface is very similar to physical adsorption, but the probability of microorganisms leaking is lower. This method requires washing the surface of the carrier with a buffer solution to obtain a hydrophilic surface that can attract the negatively charged cells or enzymes [55,56].

The procedure for immobilization is different in the case of covalent binding, because it requires the presence of a binding agent. Immobilization can be performed only on chemically activated carriers enriched with amide, ether and carbamate bonds. This

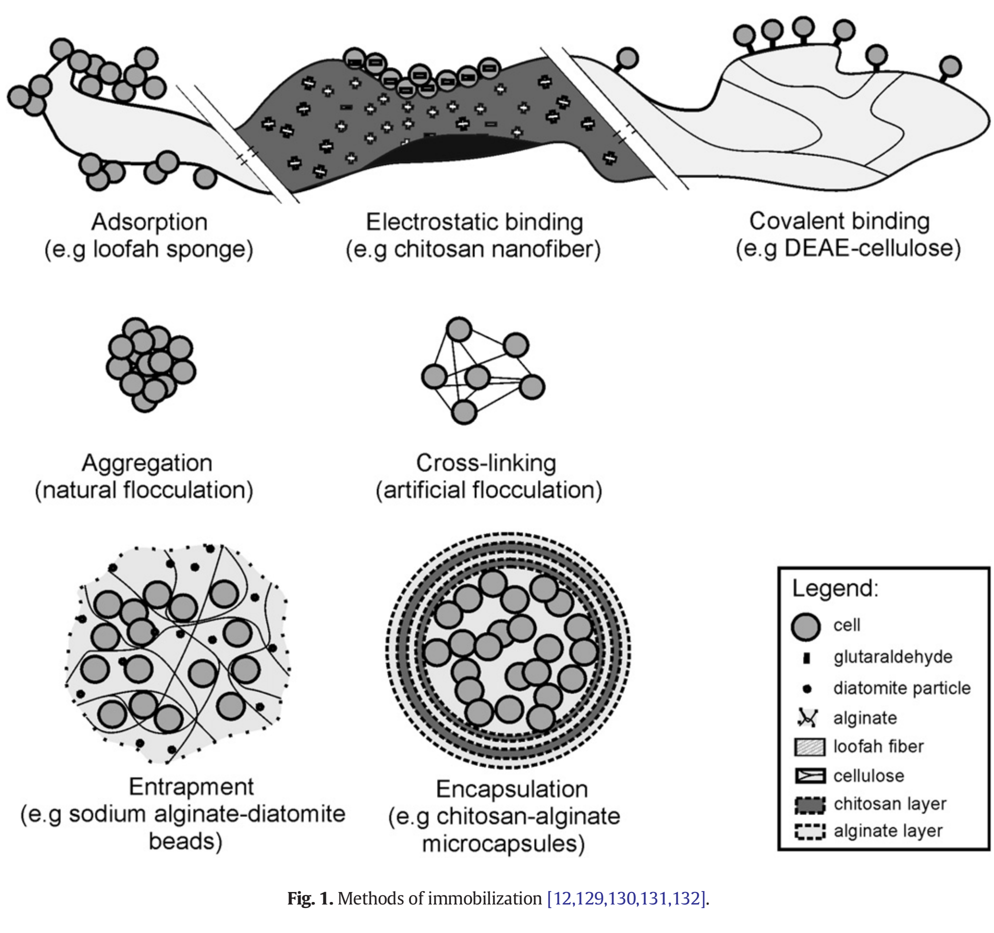

Fig. 1. Methods of immobilization [12,129,130,131,132].

method is mainly used for the immobilization of enzymes, because binding agents are often toxic to cells, and for that reason microbial viability and activity are lowered. The advantage of the covalent bonds is that they are strong enough to prevent the leaking of molecules into the environment [1,48,57,58].

3.3. Entrapment in porous matrix

Entrapment of microorganisms is well-known and widely used in bioremediation. After the entrapment, microbial cells are able to move only within a carrier. This prevents the cells from leaking into the environment but may limit the exchange of nutrients and metabolites. Microorganisms entrapped in the heterogeneous carrier are physiologically diverse. The cells located near the surface have high metabolic activity in contrast to starved cells in the interior of the carrier [1,47,51,59]. Entrapment is a rapid, nontoxic, inexpensive and versatile method [8,51]. Entrapped microorganisms are protected against environmental factors. The most important parameter in entrapment of microorganisms is the ratio of the size of the pores of the carrier to the size of the cells. In a situation where the pores are larger than the immobilized cells, they leak into the environment [1,47,51,59].

3.4. Encapsulation

Encapsulation is very similar to the entrapment, but in this case immobilized particles are separated from the external environment with a semi-permeable membrane. The biggest advantage of this method is the significant protection of biological material against the adverse conditions of the external environment. However, due to the limited permeability of the used membrane and the probability of its damage by growing cells, encapsulation is rarely used in *ex situ* bioremediation [1,47,60].

4. Support materials

Not every material is suitable for immobilization. A good carrier should be insoluble, non-toxic, both for the immobilized material and the environment, easily accessible, inexpensive, stable and suitable for regeneration. The immobilization process should be simple and harmless. Another important aspect is that different immobilization methods require carriers with specific properties. For example, carriers used for adsorption or binding on the surface should have a high porosity to ensure that the contact area of the immobilized material and the carrier is as large as possible [1,61,62]. The nature of performed bioremediation processes also has an impact on the choice of the carrier. Carriers used in bioaugmentation ought to be readily biodegradable. In wastewater treatment processes the carrier should have a high mechanical resistance because it may be exposed to different kinds of physical forces [1,63].

Carriers are classified as organic and inorganic or natural or synthetic. Natural organic carriers have many functional groups which stabilize biocatalysts. This class of carriers includes: alginate, κ-carrageenan, chitosan, sawdust, straw, charcoal, plant fibres, corncob, bagasse, rice, husks of sunflower seeds, diatomite and mycelium [64,65,66,67,68,69,70,71,72,73,74,75,76]. These supports are hydrophilic, biodegradable, biocompatible, and inexpensive because they are mostly waste from the food industry. However, the possibility of their application in bioremediation processes is limited because of low resistance to biodegradation, sensitivity to organic solvents, and stability in a narrow pH range [1,52,74,77].

Synthetic organic carriers have numerous functional groups with diversified characters. This class includes polypropylene, polyvinyl chloride, polystyrene, polyurethane foam, polyacrylonitrite and polyvinyl alcohol [78,79,80,81,82,83,84,85]. Their advantage is the possibility to regulate their structure at the macromolecular level — the selection of the proper molecular weight, the spatial structure and the manner and arrangement order of each active functional group in the chain. Moreover, during synthesis, the porosity, pore diameter, polarity and hydrophobicity of the carrier may be controlled. Furthermore, synthetic supports can be formed into various shapes (tubes, membranes, coatings, carriers of various shapes from spherical to oval), and they are easily available and relatively inexpensive [1,86,87].

Inorganic carriers (natural and synthetic) have a high chemical, physical and biological resistance. They are represented by magnetite, volcanic rocks, vermiculite, porous glass, silica-based materials, ceramics and nanoparticles [88,89,90,91,92]. A significant disadvantage of these carriers is the presence of a small number of functional groups, which prevents sufficient bonding of the biocatalyst. For that reason they are used in the formation of hybrid carriers, combining natural polymers and synthetic nanoparticles [47,88,93].

5. Immobilization in bioremediation

Higher biodegradation efficiency observed after the use of immobilized microorganisms in comparison to free ones caused the increase interest in their application in bioremediation processes [94,95]. It is assumed that carrier protects and hinders the spread of organic pollutants and in this way reduces the surface contaminants concentration on the immobilized microorganisms. Moreover, changes in microenvironment after immobilization may lead to changes in cell morphology, physiology and metabolic activity [96,97]. Wastes from the food industry are very good and inexpensive candidates for carriers [52,98,99,100,101]. Some researchers have also started to explore inorganic adsorbents, such as expanded perlite or tezontle [99,102,103]. Table 1 presents a list of carriers used in bioremediation processes.

5.1. Plant fibres

The most often applied vegetable fibre in immobilization is a sponge derived from *Luffa cylindrica* or *Luffa aegyptiaca*. These plants grow in tropical and subtropical climates. The loofah sponge shows important advantages required for immobilization processes: high porosity (85–95%) with simultaneous low density (0.018–0.05 g/cm^3). The sponge is composed of fibre networks that form an open and free space for the exchange of matter [2,104].

The first usage of the loofah sponge was reported in 2003. Microalgal-luffa sponge immobilized discs were applied in nickel biosorption processes. It has been shown that loofah sponge restricts the leaking of the immobilized biomass into the environment. It is an extremely stable carrier and can be regenerated at least 7 times [2]. Mazmanci et al. [105] reported that the loofah sponge was a source of carbon and energy for white rot fungi, and therefore should not be used for their immobilization (long-term bioremediation). On the other hand, it provides an excellent support for *in situ* or short-term bioremediation (without a source of carbon and energy) with these fungi.

5.2. Sugarcane bagasse

Sugarcane bagasse, derived from the extrusion of a plant *Saccharum officinarum*, is widely used for the production of ethanol, and is an excellent biosorbent. Bagasse is rich in carbohydrates, mainly lignin and cellulose. The spatial structure of bagasse is formed by parallel-arranged fibres and micropores (0.5–5 μm). It is an ideal place to attachment bacteria and fungal hyphae. Another advantage of this carrier is its mechanical strength. After centrifugation at 1500 rpm no disintegration or microorganism leaking into the medium were observed [100,106].

Mohammadi and Nasernejad [72] demonstrated that immobilization of *Phanerochaete chrysosporium* on sugarcane bagasse significantly

Table 1
Natural carriers used in bioremediation.

Carrier	Removed pollution	Immobilized microorganisms	Efficiency of bioremediation	References
Plant fibres (Loofah sp.)	Aromatic hydrocarbons	*Bacillus cereus*	Unimmobilized — 74% Immobilized — 79%	[122]
	Phenol	*Trametes versicolor*	Unimmobilized — 39% Immobilized — 87%	[96]
	Methyl parathion	Bacterial consortium	Unimmobilized — 55% Immobilized — 98%	[12]
	Carbendazim (pesticide)	Bacterial consortium	Unimmobilized — 12% Immobilized — 95%	[70]
	Ni	*Chlorella sorokiniana*	Unimmobilized — 64% Immobilized — 88%	[2]
Baggase	Tetradecane	*A. venetianus*	Unimmobilized — 22.3% Immobilized — 76.8%	[106]
	Anthracene	*P. chrysosporium*	Unimmobilized — 43% Immobilized — 82%	[72]
	Mesotrione (herbicide)	*Bacillus pumilus* HZ-2	Unimmobilized — 48% Immobilized — 75%	[99]
	Chromium	*Acinetobacter haemolyticus*	Unimmobilized — 38% Immobilized — 92%	[123]
Sawdust	Petroleum oil	*Arthrobacter* sp.	Unimmobilized — 18% Immobilized — 36%	[67]
	Crude oil hydrocarbon	Bacterial consortium	Unimmobilized — 79.37% Immobilized — 95.9%	[101]
	Chromium	*A. haemolyticus*	Unimmobilized — 80% Immobilized — 99.8%	[124]
Corncob	*p*-Nitrophenol	*Arthrobacter protophormiae* RKJ100	Unimmobilized — 39% Immobilized — 79%	[99]
	Carbofuran	*B. cepacia* PCL2	Unimmobilized — 67.69% Immobilized — 96.97%	[125]
	Hexadecane	*Pseudomonas* sp.	Unimmobilized — ~33% Immobilized — ~56%	[52]
	Chlorophenols	Bacterial consortium	Unimmobilized — 87% Immobilized — 89.7%	[77]
Expanded perlite	Methyl *tert*-butyl ether	Soil consortium	Unimmobilized — 22% Immobilized — 50%	[110]
	Hexadecane	*Aspergillus niger*	Unimmobilized — 81% Immobilized — 96%	[126]
	Styrene	*P. aeruginosa*	Immobilized — 90%	[111]
Tezontle	Sulfonated azo dyes (Acid Orange 7, Acid Red 8)	Bacterial consortium	Abiotic test — 16.8 mg/(L ∗ 24 h) Immobilized — 80 mg/(L ∗ 24 h)	[127]
	Propanil (herbicide)	Bacterial consortium	Immobilized — 36.78 mg/(L ∗ 24 h)	[128]
	Methyl paration	Bacterial consortium	Abiotic test — 9% Immobilized — 58%	[102]
		E. coli RAZEK	Unimmobilized — 49% Immobilized — 95%	[114]
	DDT (pesticide)	*P. fluorescens*	Unimmobilized — 55% Immobilized — 99%	[113]
Coco-peat	Oil	Bacterial consortium	Unimmobilized — 51.2% Immobilized — 86.6%	[115]
Husks of sunflower seeds	Crude oil	*Rhodococcus* sp. QBTo	Unimmobilized — 28% Immobilized — 66.1%	[74]
Cotton fibres	*n*-Heptadecane	*Acinetobacter* sp. HC8-3S	Unimmobilized — 82% Immobilized — 96%	[82]

increased the production and activity of manganese peroxidase during the biodegradation of anthracene. After the immobilization of *Acinetobacter venetianus* on this carrier, a higher rate of tetradecane degradation was observed. This was probably connected with binding of the contaminant on the hydrophobic surface of the carrier, and in consequence the easier access of microorganisms to hydrocarbon [82]. Increased efficiency of phenol degradation by immobilized *Candida tropicalis* PHB5 was also observed [100]. The microorganisms immobilized on the bagasse are suitable for bioremediation in bioreactors because they remain active for up to 8 bioremediation cycles [100,106].

5.3. Sawdust

One of the most common agro-wastes is sawdust, which has been successfully used for the immobilization of bacterial cells. *Arthrobacter* sp. immobilized on sawdust did not lose their enzymatic activity after 6 weeks of storage (at 25°C and 45°C) and was still able to degrade similar quantities of crude oil [67]. Sawdust possesses a labyrinthine structure providing very high surface area for cellular attachment. High hydrophilicity of this carrier may hamper the adsorption of oil-degrading microorganisms on the carrier. However, this difficulty may be overcome by non-toxic hydrophobic coating of sawdust [107]. Hazaimeh et al. [101] during studies on degradation of oil by a bacterial immobilized consortium, demonstrated that immobilization significantly increased the production of biosurfactants by bacteria. This was to increase the solubility, and thus the bioavailability of hydrophobic hydrocarbons.

5.4. Corncob

Materials derived from agro-industrial residues (AIR), such as corncobs, offer many advantages over synthetic matrices. Corncobs are robust, porous and perforated. This increases the attachment area for organisms and allows their growth without limiting diffusion. Corncobs have a high water holding capacity, improve soil structure and oxygen diffusion, are readily available in maize processing plants, and their usage in the processes of bioremediation provides an alternative method of AIR disposal [12,52,98].

The first study of corncobs used as a carrier in bioremediation [108] showed that they are a good carrier for the bioaugmentation of soil contaminated with oily-sludge. It was also noted that after the introduction of immobilized bacteria, the degree of oxygenation of the lower layers of the soil had increased as a result of the creation of air pockets by corncobs. Plangklang et al. [109] showed that *Burkholderia cepacia* PCL3 bacteria grow very well on the surface of the corncob, and thereby leaked into the medium due to the lack of space on the carrier. Rivelli et al. [52] observed the increased degradative activity after immobilization of bacteria on corncob powder. Additionally, this carrier stabilized soil and improved the oxygen diffusion and the water-mass transfer [52].

5.5. Expanded perlite

Volcanic rocks are known for their sorption and mechanical properties. They are widely used in construction, filters and hydroponics. One of these rocks is perlite which is excavated worldwide. Because crude perlite has a relatively high density and small surface area, it is subjected to heat treatment, resulting in a significant extension and the forming of air bubbles inside. Expanded perlite obtained in this way has a low density (0.032–0.4 g/cm^3), high porosity, and high surface area [89,110].

For the first time, expanded perlite was used for the bioremediation studies by Paca et al. [111]. It was shown that biofilter consisted of perlite particles with immobilized cells of *Pseudomonas aeruginosa* was more effective in styrene biodegradation [111]. Emtiazi et al. [112] demonstrated that the transformed cells of *Escherichia coli* immobilized on perlite were more genetically stable than in other carriers, and they were able to produce biosurfactants, which increased the solubility of petroleum hydrocarbons, and therefore the degree of their biodegradation.

5.6. Tezontle

Tezontle is a volcanic rock tested recently as a carrier in bioremediation. This rock is commonly used in Mexico as a building material, and has a characteristic reddish colour (due to the presence of iron ions). The surface is highly porous and perforated, which provides a good place for biofilm formation by microorganisms [102].

Santacruz et al. [113] demonstrated that *Pseudomonas fluorescens* immobilized on a tezontle biofilter is able to degrade DDT up to 999.8 mg/L per day and 2,4-dichlorophenoxyacetic acid up to 2634 mg/L per day. Yáñez-Ocampo et al. [103] observed biodegradation of a methyl-parathion and tetrachlorvinphos mixture by a consortium of bacteria immobilized on tezontle. They showed a decrease in the optical density of bacteria after 13 d of the experiment, whereas the death of free cells occurred after 6 d. In addition, the immobilized cells did not require supplementation with glucose during pollutant breakdown. This demonstrates that after immobilization the new environment is more friendly for bacteria which are able to degrade greater amounts of insecticides [103]. Similar results were obtained by Abdel-Razek et al. [114] during research on methyl-parathion biodegradation by transformed *E. coli* RAZEK immobilized on tezontle.

5.7. Other carriers

Recently, increasing interest is observed in the usage of coco-peat, husks of sunflower seeds and cotton fibres as carriers in bioremediation. These carriers have not gained popularity yet, but so far studies have shown their promising possibilities in bioremediation [74,82,115].

Nunal et al. [115], during the biodegradation of heavy-oil by a bacterial consortium immobilized on coco-peat, showed that the carrier, because of its porous and perforated surface, is a good place to create a stable biofilm. Moreover, they observed that the immobilized bacteria, after 60 d of the experiment, degraded 86.6% of the heavy-oil, while the free cells decomposed only 51.2% of it. After 90 d of storage, bacteria immobilized on the coco-peat had a greater survival rate than those encapsulated in sodium alginate. This makes coco-peat an excellent candidate carrier in bioaugmentation [115].

Bioremediation of crude oil by *Rhodococcus* spp. QBTo immobilized on sunflower seed husks, also shown that immobilization improves the survival and enzymatic activity of microorganisms. After 120 d of storage at 10°C the bacterial survival rate was about 76%, and therefore sunflower seed husks are an appropriate carrier for the bioaugmentation of contaminated soils [74].

Lin et al. [82] noted that the negative charge and the presence of hydroxyl and carboxylic acid groups make cotton fibres a good carrier for immobilization of microorganisms. It was shown that *Acinetobacter* sp. HC8-3S degraded more than 70% of the crude oil with 90 g/L NaCl, whereas free cells degraded about only 15% under the same conditions. This opens up the possibility of inexpensive bioremediation in areas of high salinity by immobilized microorganisms. The authors showed that the adsorption properties of cotton fibres allow the use of this carrier for the biodegradation of floating oil from oil spills [82].

5.8. Pros and cons of natural and synthetic carriers

Application of immobilized cell systems in bioremediation indicates several advantages over the usage of free microorganisms: prolonged activity, stability of biocatalyst, feasibility of continuous processing, increased tolerance to high toxic compounds concentration, easier recovery, possibility of regeneration and reuse of biocatalyst, reduction of microbial contamination risk and ability to use smaller bioreactors with simplified process [1,94,99,116]. Because each support has its own requirements in terms of the microorganisms used and the degraded compounds, the support selection is a key step which influences the success of bioremediation process [61,94].

The main feature of the carriers is mechanical resistance, which allows to the recovery, regeneration and reuse of biocatalyst in bioremediation processes [94,116,117]. This feature is typical for sawdust, wood chips, shavings, loofah sponge and polyvinyl alcohol beads, polyurethane foam, among from natural and synthetic carriers, respectively [94,96,97,117,118]. In bioremediation processes very important is the use of low-price and easy accessible carriers because only than they may be applied on the large scale. This condition fulfils plant residue, polyvinyl alcohol beads, polyurethane foam, different ceramics, and natural polymers such as agarose, κ-carrageenan, alginate, agar, and chitosan [52,62,97,103,107]. However, most of the natural polymers are non-mechanically resistant. One of the most often described natural carriers is alginate. It is cheap, biocompatible, non-toxic and easy to use [51,48,49,97,119]. Unfortunately, it cannot be used in continuous conditions because of the problems with gel degradation and low physical strength resulting in the leakage of immobilized microorganisms from the matrix [61,120].

Equally important carriers potentially useful in bioremediation have to meet other requirements of good matrices: non-toxicity and insolubility. These features characterize both natural (chitosan, loofah sponge, corncob, sawdust, tezontle, sugarcane bagasse, wood chips) and synthetic (polyvinyl alcohol, polyurethane, polypropylene, polystyrene) carriers [36,52,81,94,95,100,101,103,107,116,117,118,121].

It is possible to find among both natural and synthetic carriers almost ideal one, which may be used with success in bioremediation. However, the predominance in the usage of natural carriers is connected with their biodegradability, renewability and availability in nature. Moreover, many of natural carriers are agro-waste that may be further used in biotechnological processes. The immobilization of microorganisms on natural carriers is environmentally friendly because it causes less disposal problems that may occur for synthetic ones [52,99,100,101,107].

6. Conclusions

Interest in organic carriers, which are wastes from the agricultural and food industries, increases continuously, because they are very good material for immobilization. All of them have many functional groups, which positively affect the degree of colonization by microorganisms. Moreover, volcanic rocks (expanded perlite and tezontle) are also known as carriers which have good sorption properties and high mechanical resistance.

Carriers such as the loofah sponge and corncob have been used with success in bioremediation *in situ*, and the former has also shown the greatest support for pesticide biodegradation. In *ex situ* bioremediation the best results have been obtained using carriers such as bagasse, sawdust, expanded perlite and tezontle. Coco-peat, sunflower seed husks, cotton fibres and porous glass seem to be promising materials for immobilization, although their application requires further studies.

Conflict of interest

The authors declare no conflict of interest.

Financial support

This work was financed by the Ministry of Science and Higher Education (Poland).

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